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COMPLETE SPECIFICATION

Improvements in and relating to the Production of Metals by Electrolysis in a Fused Bath

We, HUSQVARNA VAPENFABRIKS AKTIEBOLAG, of Huskvarna, Sweden, a Swedish Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention is for a method of producing powder of the heavy metals for powder metallurgical purposes by electrolysis in a fused salt or salts of an alkali or alkaline earth metal or metals.

The invention consists in using for the electrolysis an anode containing a reducible compound of a heavy metal and a reducing agent therefor, carrying out the electrolysis at a temperature at which reduction of the reducible compound can take place but below the melting point of the metal, and depositing the metal as a powder at or on the cathode.

The process may be carried out by producing an anode from a mixture of finely divided iron ore and carbon, using tar as a binder, and using this anode for electrolysis in a fused bath of sodium and potassium chloride at a temperature of 700° C. It is believed that at this temperature the iron ore is partly reduced to lower iron oxides and to iron, and that an equilibrium is reached when only a part of the ore has been reduced to metallic iron. During the electrolysis, however, the iron formed enters the electrolyte partly as iron ions and partly as iron chloride and is transported to the cathode, and also gases (carbon monoxide and carbon dioxide) are removed. The result is that the equilibrium is disturbed in such manner that a continuous formation of metallic iron by reduction takes place. The iron is deposited on the cathode as a porous mass which in a microscope is disclosed as consisting of sharp-edged crystals.

It is known to produce magnesium and alkaline earth metals by electrolysis of their fused halides. In such a process

the halogens formed at the anode have been made to react with carbonate or oxide of magnesium or an alkaline earth metal with the formation of magnesium or alkaline earth halide, the carbonate or oxide of magnesium or an alkaline earth metal being intimately mixed with porous carbon and/or coke and/or graphite, the resulting mass being brought into the form of pieces or lumps which serve as the anode by the provision of current leads. As an improvement of this process it has been suggested that the mixture of the ore, for example magnesite or alkaline earth carbonate, with the carbon should be employed in a finely ground condition and that powdered graphite should be added to the mixture before the usual moulding, the object of this addition being to reduce the conductor resistance. The present invention on the other hand relates exclusively to the use as anode of compounds of heavy metals as starting materials and has for its object to make it possible to produce directly from these starting materials a powder suitable for powder metallurgical purposes.

In another *known* process ferric chloride in a liquid condition is subjected to electrolysis. It has been suggested in such a process to employ a ferruginous ore or the like to be converted into ferric chloride as the anode during the electrolysis of the molten ferric chloride, further to mix the ore with graphite and press the mixture into the shape of electrodes. The graphite is, however, added only to increase the conductivity of the ore, the ferric chloride sublimates at low temperatures and is unsuitable for the high temperatures required in the process of the invention for reduction purposes, and in addition, as far as can be ascertained, the known process is not one for the production of metal powders, much less metal powders suitable for powder metallurgical purposes.

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In the manner stated it is thus possible according to the present invention to produce metal powder direct from ores, for example highly concentrated ore, and metal compounds. Melting of the metal is avoided, and it is possible to use compounds or ores which are more or less impure. Sulphur, phosphorus and silicon are not transported to the cathode but are oxidised and remain in the melt or escape in the gaseous form (SiO_2 , CS_2 , SO_2 , P_2O_5 , etc.). In addition the product obtained is such that after removal of any adherent or included salt and suitable preparation it can be used as it is for powder metallurgical purposes.

Of particular importance is the production of iron and steel directly from the ore.

The powder obtained may be used as such or for powder metallurgical purposes but also for the direct production of steel. For this latter production powder metallurgical methods may be used, for example by compacting powder heated to glowing and subsequent mechanical treatment (forging, rolling, etc.) but also by extrusion with or without a subsequent mechanical treatment such as rolling, drawing, etc.

As starting materials may also be used other reducible compounds than oxide, for example sulphides and carbonates.

It is also possible to produce alloys in the powdered form, for example stainless steel, by means of the process of the invention. The alloy components may then be comprised in the same anode or separately in two or more anodes. In the latter case different voltages and/or currents may be used for different anodes.

It is further possible to produce metal carbides directly by means of the process of the invention. In the process of the invention the gases formed become positively charged and are transported to the cathode if the cathode is sufficiently near the anode. In this way carbon monoxide and carbon dioxide are brought into contact with the metal powder deposited, and if the temperature is sufficiently high carburization of the metal powder takes place. It is also possible directly to produce steel or other metals having various contents of carbon, and the carbon content may be varied by varying the conditions under which the electrolysis is carried out. In addition to the temperature the carburization is also affected by the amount of excess carbon in the anode, the distance between the anode and the cathode and the grain size of the deposited powder. It may also be of advantage to use as salt melt a salt mixture which itself is carburizing, for example a normal case

hardening bath consisting of alkali metal chlorides and alkali metal cyanides.

In order to produce hard-metals it is possible, for example, to start with cobalt oxide, tungstic acid or titanic oxide as well as a sufficient amount of carbon for reduction. By suitably choosing the temperature and the carbon content the reaction gases formed at the anode may have a sufficiently high content of carbon monoxide to carburize at the cathode those of the deposited metals which are able to form carbides. The said metals may of course be replaced by other metals used in the production of hard metals. Thus for example Ta (tantalum) may wholly or partly replace W (tungsten) and Ni may replace Co.

The electrolysis may also be conducted in such a manner that the metal powder deposited is not brought into contact with gases formed during the electrolysis so that pure metal is obtained. This result can be achieved by increasing the distance of the cathode from the anode, so that the gases evolved at the anode do not reach the cathode but escape upwards through the electrolyte.

The invention is not limited to the use of carbon as reducing agent. Thus for example chromium oxide can be reduced only with difficulty, and in such a case it may be preferable to use, i.e. mix into the anode, aluminium powder, which reduces the chromium oxide to metallic chromium, which in turn is electrolytically transported to the cathode. This process leads to formation of aluminium oxide which one way or the other should be removed from the melt, for example by circulating the electrolyte through a filter. Such a reducing agent as aluminium may be used also for the reduction of titanium oxide.

In certain cases it may be of advantage to mix into the anode turnings or other materials for the purpose of increasing the strength of the anode and/or the porosity. In general it is desirable that the anodes should have a certain degree of porosity in order to facilitate the escape of gases formed as a result of the reduction.

The anodes may be made from a mixture of a metal compound, a reducing agent and a binding agent, for example tar. The mixture is compressed into rods which are subjected to heat treatment at elevated temperatures, for example at a temperature of 150–300° C., when a rod is obtained having a strength of the same order as graphite. The anodes may also be made by the Söderberg method. According to this method the material, of which the anodes are to be made, is

packed into metal tubes, which are immersed in the fused bath. The material is advanced down into the melt and dried and sintered part by part.

5 As regards the composition of the bath the halides of the alkali or alkaline earth metals are suitable from a practicable point of view. The chlorides and fluorides of the metals sodium, potassium, lithium 10 and calcium have been found particularly suitable. A small addition of salts of the metals to be produced in the powdered form generally has the effect of increasing the grain size of the powder deposited. 15 The method is, however, not limited to the use of halides, and it is possible to use for example cyanides, borates, phosphates etc., of the alkali or alkaline earth metals in suitable mixtures.

20 In the tests carried out the temperature has varied between 500 and 900° C., but the invention is not in any way limited to this temperature range. The temperature used depends on the metal to be produced in the powdered form, on the grain size desired and other factors. For the reduction of iron with carbon the most suitable temperature range seems to be from 600 to 900° C.

30 The mass deposited on the cathode may be removed by means of scrapers, by using rotating cathode and in similar or other ways. The mass removed can be ground and washed for removal of the salt. It is also possible to remove the cathode from the bath, allow the excess of molten salt to run off and dip the still glowing cathode into cold water. In this way the layer of metal powder is completely exploded, so that the crystals are obtained as a powder. The cathodes may be made of thin sheets which easily can be extracted from the bath to be immersed in water. The vessel in which the electrolysis is carried out may be connected with the cathode or may itself form the cathode.

In the following some of the tests carried out are described.

50 EXAMPLE 1. PRODUCTION OF STEEL POWDER I.

Finely disintegrated ore was mixed with so much finely ground graphite that the latter was present in an excess of 20% 55 above the amount theoretically required for reduction of the ore to iron under formation of carbon monoxide. Then in a mixing machine this charge of ore and carbon powder was intimately mixed with mineral coal tar. The mixture was compacted into a round rod which was heated to about 200° C. The electrolysis vessel, which also served as cathode, was charged

with a mixture of 44% sodium chloride and 56% potassium chloride and heated to about 700° C. The anode was placed in the centre of the vessel. At first coloured tar products were evolved and escaped. When the temperature of the anode had risen to about 650° C. formation of carbon monoxide and carbon dioxide took place. The electrolysis was then started and the formation of gases increased very considerably. The test lasted two hours and the cell voltage 1.3—1.7 volts. The amount of powder obtained, after washing, was 38.5 grams, the current yield was 92.6% calculated on the assumption that the iron deposited was bi-valent, and the content of carbon in the powder was 1.2%. After the termination of the electrolysis the anode was covered with a fine powder of carbon which showed that the excess of carbon had been unnecessarily great. 85

EXAMPLE 2.

PRODUCTION OF STEEL POWDER II.

The same anode and the same general arrangement as in Example 1 was used except that iron chloride and magnesium chloride were added to the salt melt. A coarse-grained powder was obtained, resembling fine sea sand. The carbon content of the powder was 0.9%. 90

EXAMPLE 3.

PRODUCTION OF STEEL POWDER III.

The same anode and the same general arrangement as in Example 1 was used except that the distance between the anode and the cathode was less. The carbon content of the powder was 1.5%. 95 100

EXAMPLE 4.

PRODUCTION OF NICKEL.

Carbon and nickel oxide in the proportions of 16% carbon and 84% nickel oxide were mixed, using tar as binder, and formed to an anode, which was heat treated at 200—300° C. to increase the strength. The anode was used for electrolysis in a self melt containing 44% NaCl and 56% KCl, at a temperature of 670—700° C. The metal powder, which was very pure and finely crystalline, did not adhere to the cathode but fell to the bottom of the electrolysis vessel where it collected. The current yield was 97.5%. On account of the comparatively high ohmic resistance of the anode the cell voltage was 3.2—3.8 volts. If the graphite used is replaced by graphite having better conducting properties, for example tar graphite, the resistance of the anode can be lowered and thus also the cell voltage. 105 110 115 120

EXAMPLE 5.

PRODUCTION OF CHROMIUM POWDER.

Chromium oxides and graphite were mixed and compacted as described above. The temperature used was 800—850° C. The bath was made up of 44% sodium chloride and 56% potassium chloride. The current was 13—15 amperes, the cell voltage 2—3 volts. The powder obtained was very fine-grained. Chromium carbide can be made in a similar manner by using such a small distance between the anode and the cathode that the carburizing gases (CO₂, CO) generated at the anode reach the cathode and carburize the metal deposited on the cathode.

The process can of course be carried out in the presence of an inert or reducing atmosphere but this, at least in some cases, is not necessary, and the tests described above have been carried out without taking this precaution.

The amount of reducing agent may vary and is not limited to an excess of 20%.

The term "metal" also includes alloys, for example alloys between metals (for example stainless steel) and alloys with carbon (for example steel and carbides).

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of producing powder of the heavy metals for powder metallurgical purposes by electrolysis in a fused salt or salts of an alkali or alkaline earth metal or metals, consisting in using for the electrolysis an anode containing a reducible compound of a heavy metal and a reducing agent therefor, carrying out the electrolysis at a temperature at which reduction of the reducible compound can take place but below the melting point of the metal, and depositing the metal as a powder at or on the cathode.

2. A method as claimed in claim 1, characterised in that the electrolysis is carried out with an anode, which is made of a mixture of finely divided reducible compound of a heavy metal, a finely divided reducing agent and a binder, shaped and heat-treated.

3. A method as claimed in claim 1, characterised in that the electrolysis is carried out with an anode comprising a

mixture of a finely divided reducible compound of a heavy metal and a finely divided reducing agent, with or without the addition of a binder, discontinuously or continuously advanced down into the melt.

4. A method as claimed in any of claims 1 to 3 for the production of alloys, characterised in that the electrolysis is carried out with an anode, which contains all the metallic alloying components which are to be contained in the powder produced.

5. A method as claimed in any of claims 1 to 3 for the production of alloys, characterised in that the electrolysis is carried out with two or more anodes containing different alloying components, the anodes optionally being supplied with different voltages and/or current densities.

6. A method as claimed in any of claims 1—5 for the production of metal carbides, characterised in that carburisation takes place at the cathode by means of carbon-containing gases generated at the anode as the result of the reduction.

7. A method as claimed in any of claims 1—6, characterised in that the electrolysis is carried out with an anode, which contains material, for example turnings, for increasing the strength and/or the porosity of the anode.

8. A method as claimed in any of claims 1—7, characterised in that the electrolysis is carried out in a bath containing one or more molten halides, cyanides, borides, or phosphates of the alkali or alkaline earth metals.

9. A method as claimed in claim 1, characterised in that the electrolysis for the production of iron and steel, using carbon as reducing agent, is carried out at a bath temperature of 600—900° C.

10. A method as claimed in any of claims 1—9, characterised in that the powder obtained is subjected to further treatment according to powder metallurgical methods, for example for the direct production of steel.

11. A method substantially as described.

12. Metal powder when produced by the method claimed in any of claims 1—11.

Dated this 13th day of December, 1946.
HUSQVARNA VÄPENTÄBRIKS

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